
III.B.4 Reformer for Conversion of Diesel Fuel into CO and Hydrogen

Objectives for Phase I

- Develop low-cost catalysts for use in catalytic membrane reactors for the near complete conversion of commercial diesel fuel into H₂ and CO.
- Demonstrate catalyst tolerance to sulfur contained in commercial diesel fuel at levels of 200 ppm by mass.
- Demonstrate long-term catalytic activity (>1,450 hours) at 1,000°C for reforming commercial diesel fuel.

Approach

- Operate catalysts under conditions which thermodynamically favor formation of H₂ and CO and which completely suppress formation of carbon.
- Choose catalytic materials which do not form thermodynamically stable bulk sulfides under desired reactor operating conditions.
- Develop perovskite-based catalysts for catalytic membrane reactor walls and for catalyst beds which provide highly mobile and reactive oxygen in a dissociated form.

Accomplishments

- Synthesized and tested over 40 catalyst formulations.
- Demonstrated 80-99% conversion of diesel fuel at 1,000°C into H₂, CO, CO₂ and CH₄ for the most active perovskite-based catalysts.
- Demonstrated stable diesel fuel reforming catalytic activity at 1,000°C for two months for one preferred perovskite-based catalyst formulation using commercial diesel fuel containing 200 ppm by mass sulfur.

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Future Directions for Phase II and Beyond

- Will incorporate catalysts onto walls of catalytic membrane reactors to form self-cleaning systems for the elimination of carbon build-up on reactor walls in the cool zones (250 to 950°C) of diesel fuel reformers.
- Will further optimize perovskite-based catalysts for high temperature stability (1,000°C) as well as for use on reactor walls operated in the cooler reactor regions in which the diesel fuel is injected and heated to the preferred reaction temperature.

Introduction

It is desired to convert the hydrocarbons of commercial diesel fuel into a mixture of hydrogen and carbon monoxide which can be used to power solid oxide fuel cells. Thermodynamic calculations summarized in Figure 1 predict that this can be accomplished for stoichiometric mixtures containing one mole of atomic oxygen for each mole of carbon in the diesel fuel if the system is brought to equilibrium at temperatures near 1,000°C. If catalysts are to be used to increase rates of reaction, then the catalysts must be capable of adsorbing and dissociating molecular oxygen into highly active atomic oxygen in order to oxidize the more stable aromatic components of diesel fuel. Catalysts must be stable to at least 1,000°C. Furthermore, catalysts must be tolerant to the sulfur present in commercial diesel fuel.

Thermodynamics also predicts (see Figure 1) that formation of carbon will be highly favored at lower temperatures (300-950°C). A major issue in diesel fuel reformers is the deposition of carbon onto reactor walls as the diesel fuel is heated from ambient temperatures to the desired reforming temperature. The carbon, growing on reactor walls and deposited onto catalyst beds, can rapidly plug fuel reformers. Formation of carbon can be suppressed by addition of steam, CO₂, hydrogen or excess oxygen, but these options lead to reduction of overall fuel cell system efficiencies.

Approach

To eliminate carbon deposition onto the reactor walls in the cool zones of the diesel fuel reformer, without adversely lowering the overall system efficiency by adding excess oxygen, a catalytic membrane reactor is proposed. In such a device (see Figure 2), walls

Thermodynamic Equilibrium Calculations for Reforming Diesel Fuel into CO + H₂ by Partial Oxidation

H : C : O Ratios Adjusted to 1.86 : 1 : 1

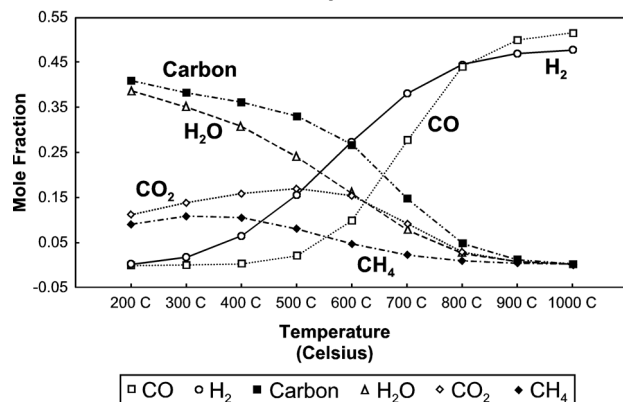


FIGURE 1. Results of thermodynamic calculations predicting that diesel fuel can be converted into the desired hydrogen and carbon monoxide if one mole of oxygen is added for each mole of carbon in the fuel and if the system is brought to equilibrium near 1,000°C. Calculations also predict formation of carbon as diesel fuel is heated to the desired reforming temperature.

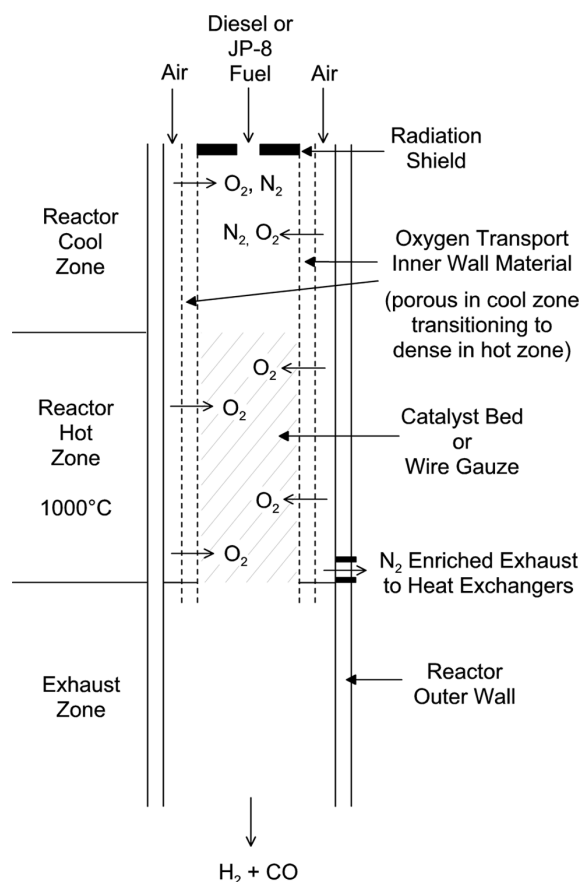


FIGURE 2. Schematic showing the concept of a catalytic membrane reactor in which walls of the reformer are catalytic and provide dissociated oxygen for suppression of deposition of carbon in the reactor cool zones. Reactor walls are self-cleaning.

of the reformer are catalytic and locally provide very high concentrations of atomic oxygen for suppression of the deposition of carbon. The novel feature of the technology is that the reactor walls are essentially self-cleaning, diffusing and effusing oxygen from the outer reactor wall to the inner reactor wall. Oxygen is kept at very high local concentrations near the inner reactor walls, where it is needed to suppress formation of carbon at low temperatures, while the overall concentration of oxygen in the reactor system is kept close to the 1 to 1 ratio of carbon to oxygen required by thermodynamics and for high overall system efficiency.

The catalytic membrane reactor requires very active catalysts for the dissociation of molecular oxygen and for the transport of atomic oxygen into the cool zones of the reactor. Very stable catalysts operating at 1,000°C in the hot zone of the fuel reformer are also required.

Results

Some 40 catalyst formulations were fabricated and tested for activity and stability in reforming commercial diesel fuel containing approximately 200 parts per million by weight sulfur. A number of catalysts with the perovskite crystal structure were designed for high mobility of dissociated oxygen both in the bulk and on the catalyst surface. The perovskite catalysts contained low-cost transition metals which were predicted not to form thermodynamically stable bulk metal sulfides under desired fuel reforming operating conditions. A number of perovskite-based oxidation catalysts showed excellent diesel fuel reforming activity (see Figure 3), exceeding that of Pt-Rh catalysts supported on YSZ.

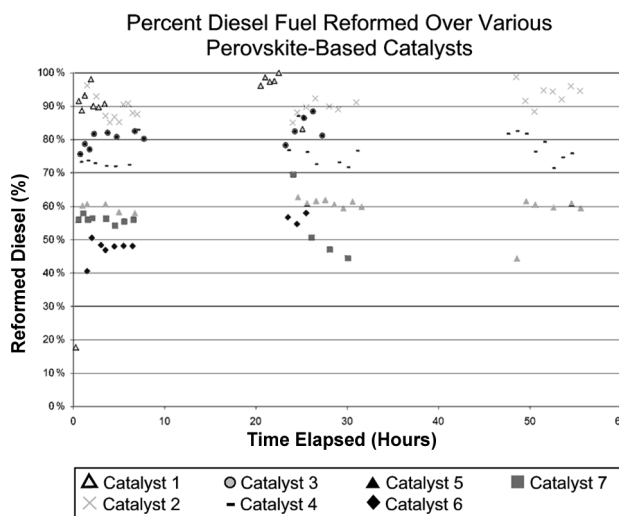


FIGURE 3. Percent of commercial diesel fuel converted into CO, CH₄ and CO₂ for various catalysts operated at 1,000°C. A number of perovskite-based catalysts showed activity superior to Pt-Rh supported on yttria-stabilized zirconia.

Theoretical analysis indicated that a platinum-rhodium gauze would form a near-ideal catalyst in the hot zone. Molecular oxygen is readily adsorbed and dissociated on Pt-Rh surfaces, providing very reactive atomic oxygen. Wire gauzes exposed to diesel fuel and oxygen can operate well above 1,000°C (white-hot) at temperatures for which thermodynamics overwhelmingly favors formation of H_2 and CO and at which sulfides of platinum and rhodium are not stable. However, the cost of platinum-rhodium gauze is prohibitive for most non-military commercial applications. Finely dispersed Pt-Rh supported on yttria-stabilized zirconia (in which the oxides support provides mobile dissociated oxygen as in solid oxide fuel cells) functioned well as a diesel reforming catalyst, but was not stable in long-term tests at 1,000°C due to sintering of the Pt-Rh crystallites (see Figure 4).

The more active perovskite-based catalysts appear to be adequate for use in the cool zones of catalytic membrane reactors (see Figure 3). The preferred perovskite-based catalyst showed stable diesel fuel reforming activity for two months at 1,000°C for commercial diesel fuel containing 200 ppm by mass sulfur (see Figure 4), and should be adequate for use in the catalyst bed of the reformer hot zone.

Conclusions and Future Directions

Catalysts were developed, based upon oxides with the perovskite crystal structure, which showed high catalytic activity for reforming high-sulfur (200 ppm by mass) commercial diesel fuel into H_2 and CO at 1,000°C. Incorporation of these catalysts into catalytic membrane reactors will allow development of fuel

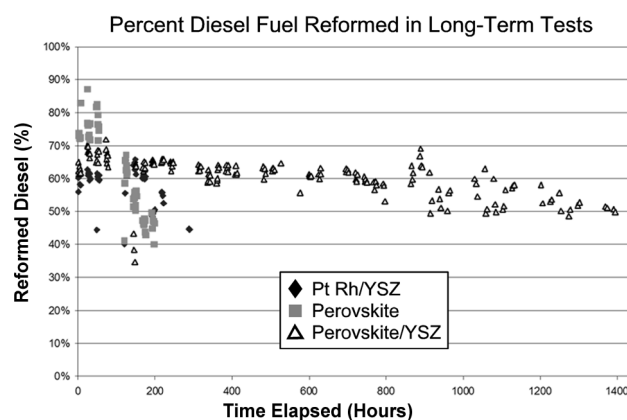


FIGURE 4. Long-term test (>1,450 hours) at 1,000°C, with commercial diesel fuel containing 200 ppm by mass sulfur, showing superior stability of a perovskite-based catalyst relative to Pt-Rh supported on yttria-stabilized zirconia.

reformers with novel self-cleaning reactor walls sufficient for suppression of deposition of carbon in reactor cool zones while minimizing addition of oxygen and maximizing overall system efficiency desired for solid oxide fuel cells. In future work, the catalysts will be incorporated into the walls of catalytic membrane reactors and used for reforming of commercial diesel fuel and JP-8.

FY 2006 Publications/Presentations

1. "Oxygen Membrane Catalytic Fuel Reforming," NETL SECA Fuel Processing Workshop, December 6, 2005, Pittsburgh, Pennsylvania.